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Controlled Rotary Motion of Light-driven Molecular Motors Assembled on a Gold Film

Gregory T. Carroll, Michael M. Pollard, Richard van Delden and Ben L. Feringa*

Supporting Info

General remarks

General remarks for synthetic procedures:

Reagents were purchased from Aldrich, Acros, Strem, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. All reactions were performed in oven- or flame-dried round bottomed or modified Schlenk (Kjeldahl shape) flasks fitted with rubber septa under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation 30–40°C. Flash column chromatography was performed as described by Still et al.¹ Chromatography: silica gel, Merck type 9385 230-400 mesh. TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or exposure to ceric ammonium molybdate solution (CAM) or an acidic solution of *p*-anisaldehyde (anisaldehyde) followed by brief heating with a heating gun. Mass spectra (HRMS) were recorded on an AEI MS-902. ¹H and ¹³C NMR spectra were recorded on a Varian VXR-300 a Varian Mercury Plus, or a Varian Inova 500 operating at 299.97, 399.93, and 499.98 MHz, respectively, for the ¹H nucleus, and at 75.43, 100.57 and 124.98 MHz for the ¹³C nucleus.

Spectroscopy (NMR, CD, IR).

Chemical shifts for protons are reported in parts per million scale (L scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents (CHCl₃: δ 7.26, C₆D₅H: δ 7.15, CD₂HCO₂D: δ 3.31, CD₂HCN δ 1.93). Chemical shifts for carbon are reported in parts per million (L scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (CDCl₃: δ 77.0, C₆D₆: δ 128.0, D₃CO₂D: δ 44.9). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant in Hz, and assignment. CD spectra were recorded using a Jasco J715 spectropolarimeter and a JASCO PFD-350S/350L Peltier-type FDCC attachment with a temperature control with a 1.0 cm cell with the following conditions: speed 100 nm/min, response time, 1 s; bandwidth 1 nm (solution) or 10 nm (surface). IR spectroscopy was performed with a Perkin Elmer IR spectrometer (Spectrum 400). RAIR spectra of the monolayers of motors were obtained using a Spectrum 400 FT-IR (Perkin Elmer) equipped with a Pike Veemax II attachment and a liquid nitrogen cooled MCT detector. Grazing angle spectra were taken with parallel-polarized light and an incident reflection

angle of 80°. Spectra of SAMs were measured on quartz substrates bearing approximately 5 nm Au films. The spectra were compared with the spectrum of the free motor obtained using an UATR attachment containing a ZnSe crystal.

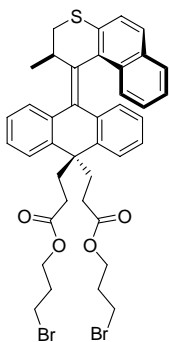
Atomic Force Microscopy (AFM)

AFM images were obtained with a PicoScan LE (Molecular Imaging) atomic force microscope in tapping mode. Tips with a force constant of approximately 5 N/m were used. Images were scanned at rates ranging from 1-2 lines per second.

Synthesis of molecular motors with thiol-terminated tethers for attachment to the gold surfaces.

Synthetic procedures

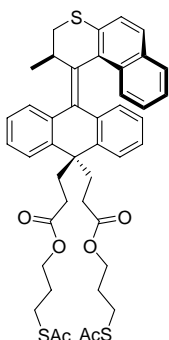
Bis(3-bromopropyl) 3,3'-(10-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-9,10-dihydroanthracene-9,9-diyl)dipropionate S1



Oxalyl chloride (200 μ l) was added to a solution containing the reported diacid analogue of **1**² (160 mg, 0.300 mmol) in CH_2Cl_2 (4 mL). DMF (1 drop, ca. 20 μ L) was added, and the mixture heated to reflux with stirring for 2 h. The mixture was then concentrated to dryness *in vacuo*, redissolved in CH_2Cl_2 (1 mL), and again concentrated to dryness *in vacuo*. To this mixture was added CH_2Cl_2 (3 mL), 3-bromo-pentanol, and pyridine, and the mixture stirred for 6 h at rt. The mixture was concentrated *in vacuo*, and purified by flash chromatography (heptane:EtOAc, 5:1) to give the diester as a colorless glass (232 mg, 70 %).

¹H NMR (300 MHz, CDCl_3) δ 0.78 (6H, d, J = 6.6 Hz), 1.90-2.22 (4H, m), 2.30-2.90 (4H, m), 2.99 (1H, dd, J = 2.7, 11.7 Hz), 3.39 (2H, t, J = 6.4 Hz), 3.40 (2H, t, J = 6.4 Hz), 3.65 (1H, dd, J = 8.8, 11.6 Hz), 4.20 (2H, t, J = 6.0 Hz), 4.21 (2H, t, J = 6.0 Hz), 4.30-4.40 (1H, m), 6.24 (ABX 1H, dd, J_{app} = 1.4, 7.8 Hz), 6.30 (ABX 1H, t, J_{app} = 7.2 Hz), 6.86 (1H, dt J = 1.4, 7.6 Hz), 6.91 (1H, t, J = 7.6 Hz), 7.16 (1H, t, J = 7.6 Hz), 7.24 (app. 2H, t, J = 7.4 Hz), 7.32-7.43 (2H, m), 7.50 (1H, d, J = 8.4 Hz), 7.55 (1H, dd, J = 1.4, 7.8 Hz), 7.65 (1H, d, J = 8.0 Hz), 7.68 (1H, d, 8.4 Hz), 7.77 (1H, dd, J = 1.6, 7.2 Hz); ¹³C NMR (75 MHz, CDCl_3) δ 173.6, 173.0, 142.6, 137.9, 137.7, 137.1, 136.4, 135.3, 134.4, 131.9, 131.3, 130.6, 128.3, 128.3, 127.9, 127.4, 127.3, 126.9, 126.1, 125.7, 125.4, 125.1, 124.9, 124.6, 124.3, 62.4, 62.2, 46.5, 37.8, 37.2, 34.72, 31.65, 31.9, 30.4, 29.5, 29.35, 29.29, 20.7; HRMS calcd for $\text{C}_{40}\text{H}_{40}\text{O}_4\text{SBr}_2$ 774.1013, found 774.1015.

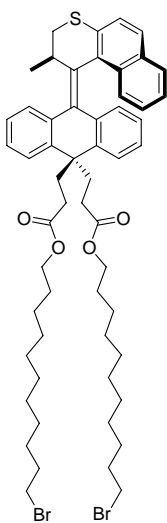
Bis(3-(acetylthio)propyl)3,3'-(10-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-9,10-dihydroanthracene-9,9-diyl)dipropionate S2



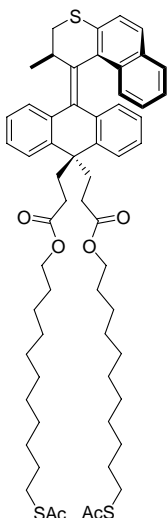
KSAC (43 mg, 0.30 mmol) was added to a solution of dibromide **S1** (77 mg, 0.10 mmol) in DMF (1 mL). The mixture was stirred under inert atmosphere for 24 h, then diluted with water (5 mL), and extracted with EtOAc (2 x 5 mL). The combined organic fractions were washed with

water (4 x 4 mL), brine, dried (Na₂SO₄) and reduced *in vacuo* to give an amber oil. Flash chromatography (3:1, Hex:EtOAc, R_f = 0.34) gave the product as a colourless gum (52 mg, 68 %). The enantiomers were resolved using Chiralcel OD eluting at 1 mL/min (analytical) or 15 mL/min (preparative column) with Heptane:ⁱPrOH, 93:7. The enantiomers eluted at 22.7 and 25.1 min (analytical column) or 18 min and 22 min (preparative). ¹H NMR (400 MHz, CDCl₃) δ 0.77 (6H, d, *J* = 6.4 Hz), 1.79-1.91 (5H, m), 1.92-2.13 (2H, m), 2.27-2.39 (1H, m), 2.29 (3H, s), 2.31 (3H, s), 2.52 (2H, dquin, *J* = 3.2, 12.7 Hz), 2.61-2.73 (2H, m), 2.79-2.84 (1H, m), 2.89 (4H, t, *J* = 6.8 Hz), 2.99 (1H, dd, *J* = 3.2, 12.0 Hz), 3.01 (1H, t, *J* = 6.4 Hz), 3.61-3.69 (2H, m), 4.11 (4H, dt, *J* = 2.2, 6.0 Hz), 4.29-4.37 (1H, m), 6.21 (1H, ABX dd, *J*_{app} = 1.4, 7.8 Hz), 6.30 (1H, ABCX dt, *J*_{app} = 1.2, 7.6 Hz), 6.83 (1H, dt, *J* = 1.6, 7.6 Hz), 6.89 (1H, dt, *J* = 1.2, 7.6 Hz), 7.15 (1H, dt, *J* = 1.0, 7.4 Hz), 7.21 (1H, d, *J* = 8.0 Hz), 7.32-7.43 (2H, m), 7.49 (1H, d, *J* = 8.4 Hz), 7.55 (1H, dd, *J* = 1.2, 8.2 Hz), 7.65 (1H, d, *J* = 8.0 Hz), 7.67 (1H, d, 8.4 Hz), 7.75 (1H, dd, *J* = 1.4, 7.6 Hz); ¹³C NMR (APT, 100 MHz, CDCl₃) δ 195.4 (2X), 173.7, 173.1, 142.6, 137.8, 137.7, 137.0, 136.2, 135.2, 134.4, 131.9, 131.2, 130.6, 128.2, 128.2, 127.8, 127.4, 127.3, 126.8, 126.1, 125.6, 125.5, 125.4, 125.1, 124.8, 124.6, 124.3, 63.0, 62.8, 46.4, 37.9, 37.2, 34.6, 30.58, 30.56, 30.4, 29.5, 28.6, 28.6, 28.3, 25.63, 25.59, 20.7) (NB the two absorptions from the thioester carbonyls overlap); HRMS (EI) calcd for C₄₄H₄₆O₆S₃ 766.2456, found 766.2467.

Bis(11-bromoundecyl)3,3'-(10-(2-methyl-2,3-dihydro-1H-benzof[*f*]thiochromen-1-ylidene)-9,10-dihydroanthracene-9,9-divl)dipropionate S3



SOCl₂ (2 mL) was added to a stirred solution of the diacid analogue of **1** (150 mg, 0.28 mmol) and DMF (1 drop) in CH₂Cl₂ (5 mL), and the mixture heated to reflux for 2 h. The mixture was concentrated *in vacuo*, and the residue dissolved in CH₂Cl₂. The mixture concentrated *in vacuo* again, dissolved in CH₂Cl₂ (2 mL) and treated with 11-bromoundecanol (211 mg, 0.84 mmol) and Et₃N (101 mg, 1.00 mmol) for 14 h. This mixture was concentrated, and purified by flash chromatography (9:1; Heptane:EtOAc) to give the dibromoester as a colourless oil (167 mg, 60%). ¹H NMR (400 MHz, CDCl₃) δ 0.73 (3H, d, *J* = 6.8 Hz), 1.04-1.28 (28H, m), 1.29-1.40 (4H, m), 1.42-2.58 (4H, m), 1.78 (4H, dquin, *J* = 1.0, 7.2 Hz), 1.79-2.05 (2H, m), 2.20-2.32 (1H, m), 2.48 (2H, dpent, *J* = 2.8, 13.9 Hz), 2.55-2.70 (2H, m), 2.95 (1H, dd, *J* = 3.0, 11.8 Hz), 3.34 (2H, t, *J* = 6.8 Hz), 3.35 (2H, t, *J* = 6.8 Hz), 3.61 (1H, dd, *J* = 8.8, 7.6 Hz), 3.99 (4H, dt, *J* = 2.1, 6.6 Hz), 4.25-4.32 (1H, m), 6.82 (1H, dt, *J* = 1.6, 8.0 Hz), 6.91 (1H, d, *J* = 7.2 Hz), 7.14 (1H, ddd, *J* = 7.8, 6.8, 0.8 Hz), 7.21 (1H, t, *J* = 7.2 Hz), 7.32-7.42 (2H, m), 7.49 (1H, d, *J* = 8.0 Hz), 7.54 (1H, d, *J* = 7.6 Hz), 7.64 (1H, d, *J* = 8.0 Hz), 7.68 (1H, d, *J* = 8.8 Hz), 7.75 (1H, dd, *J* = 7.2, 1.6 Hz); ¹³C NMR (APT, 100 MHz, CDCl₃) δ 173.9, 173.3, 142.8, 137.8, 137.0, 136.2, 135.2, 134.4, 131.9, 131.2, 130.6, 128.2, 127.8, 127.7, 127.4, 127.2, 126.8, 126.0, 125.5, 125.1, 124.7, 124.5, 124.4, 64.7, 64.6, 46.5, 38.1, 37.2, 34.6, 34.0, 32.8, 30.6, 29.6, 29.3, 28.68, 28.66, 28.59, 28.5, 28.2, 28.1, 25.9, 20.7; ES MS (M+Li) 1007.4



Bis(11-(acetylthio)undecyl) 3,3'-(10-(2-methyl-2,3-dihydro-1H-benzo[f]thiochromen-1-ylidene)-9,10-dihydroanthracene-9,9-diyl)dipropionate S4

A solution of dibromo-olefin **S3** (60 mg, 0.060 mmol) and KSAc (35 mg, 31 mmol) in DMF (3 mL) was stirred overnight, diluted with EtOAc, and washed with water (5 x 10 mL), brine (3 mL), dried (Na₂SO₄) and the solvents removed *in vacuo* to give an amber residue, which was purified by flash chromatography (8/1; Heptane/EtOAc) to give a light yellow oil (33 mg, 55%). The enantiomers were separated on a Chiralpak AD eluting at 0.1 mL/min, Enant 2 at 15.7 min. ¹H NMR (400 MHz, CDCl₃) δ 0.77 (3H, d, *J* = 6.4 Hz), 1.10-1.35 (28H, m), 1.47-1.62 (8H, m), 1.90-2.10 (2H, m), 2.31 (3H, s), 2.32 (3H, s), 2.40-2.72 (3H, m), 2.78-2.85 (1H, m), 2.846 (2H, t, *J* = 8.0 Hz), 2.849 (2H, t, *J* = 8.0 Hz), 2.95-3.05 (1H, m), 3.66 (1H, t, *J* = 10.4 Hz), 4.03 (2H, t, *J* = 6.6 Hz), 4.04 (2H, t, *J* = 6.8 Hz), 4.31-4.38 (1H, m), 6.21 (1H, ABX dd, *J* = 1.0, 80 Hz) 6.28 (1H, ABXY ddd, *J* = 0.8, 8.0, 8.0), 6.82 (1H, dt, *J* = 1.2, 7.6 Hz), 6.91 (1H, dt, *J* = 1.2, 7.8 Hz), 7.13 (1H, t, *J* = 7.4 Hz), 7.21 (2H, app. t, *J* = 7.0 Hz), 7.30-7.43 (2H, m), 7.49 (1H, d, *J* = 8.4 Hz), 7.54 (1H, d, *J* = 7.2 Hz), 7.64 (1H, d, *J* = 7.6 Hz), 7.67 (1H, d, *J* = 8.4 Hz), 7.75 (1H, dd, *J* = 1.6, 7.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 196.8, 173.9, 173.3, 142.9, 137.8, 137.0, 136.2, 135.2, 134.4, 131.9, 131.2, 130.6, 128.3, 128.2, 127.8, 127.4, 127.3, 126.8, 126.0, 125.6, 125.5, 125.1, 124.7, 64.8, 64.7, 46.5, 38.1, 37.2, 34.6, 30.65, 30.58, 29.6, 29.5, 29.43, 29.41, 29.40, 29.37, 29.20, 29.18, 29.12, 29.06, 29.0, 28.8, 28.6, 28.6, 25.9, 25.9, 20.7; ES MS (*M*+Li) 997.6.

Preparation of Semi-transparent Gold Films

Quartz substrates were made adhesive towards gold by coating with aminopropylmethyldiethoxysilane (synthesized by a reported procedure³) by immersion in a 1 mM solution in freshly distilled toluene for 12 h followed by copious rinsing of the substrate with toluene and methanol and sonication in toluene, methanol and toluene:methanol 1:1 2 min each. Gold films were prepared by vapor deposition onto the quartz surfaces modified with aminopropylmethyldiethoxysilane using an Edwards Thermal evaporator. Both sides of the substrate were coated using a rotating sample holder. Deposition was carried out in a vacuum in the 10⁻⁶ torr range and at a rate of 0.1 nm/s. The deposition thickness was monitored using a calibrated frequency thickness monitor. The film thickness on each side of the substrate was estimated to be half the total amount of gold deposited on the thickness monitor.

Self-assembly of 3 and 4 onto Gold Films

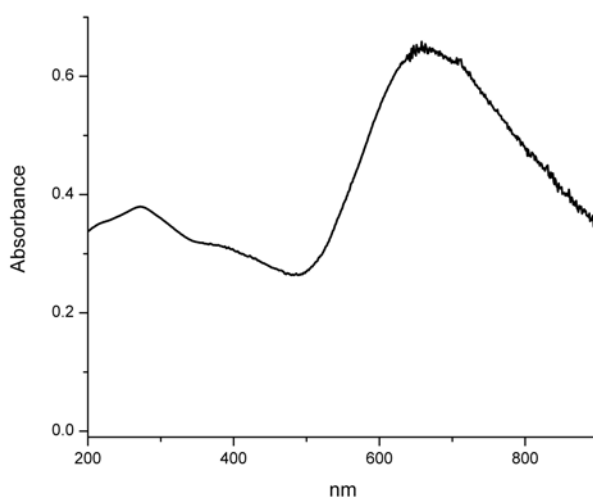
Gold surfaces were immersed in 10 mM solutions of **2** or **3** in distilled toluene for approximately 15 h. Mixed surfaces were prepared by addition of 10 equiv of dodecanethiol to the motor solution. After removal from solution the surfaces were rinsed with copious amounts of toluene and sonicated three times for two minutes each in toluene.

Preparation of Gold Colloids

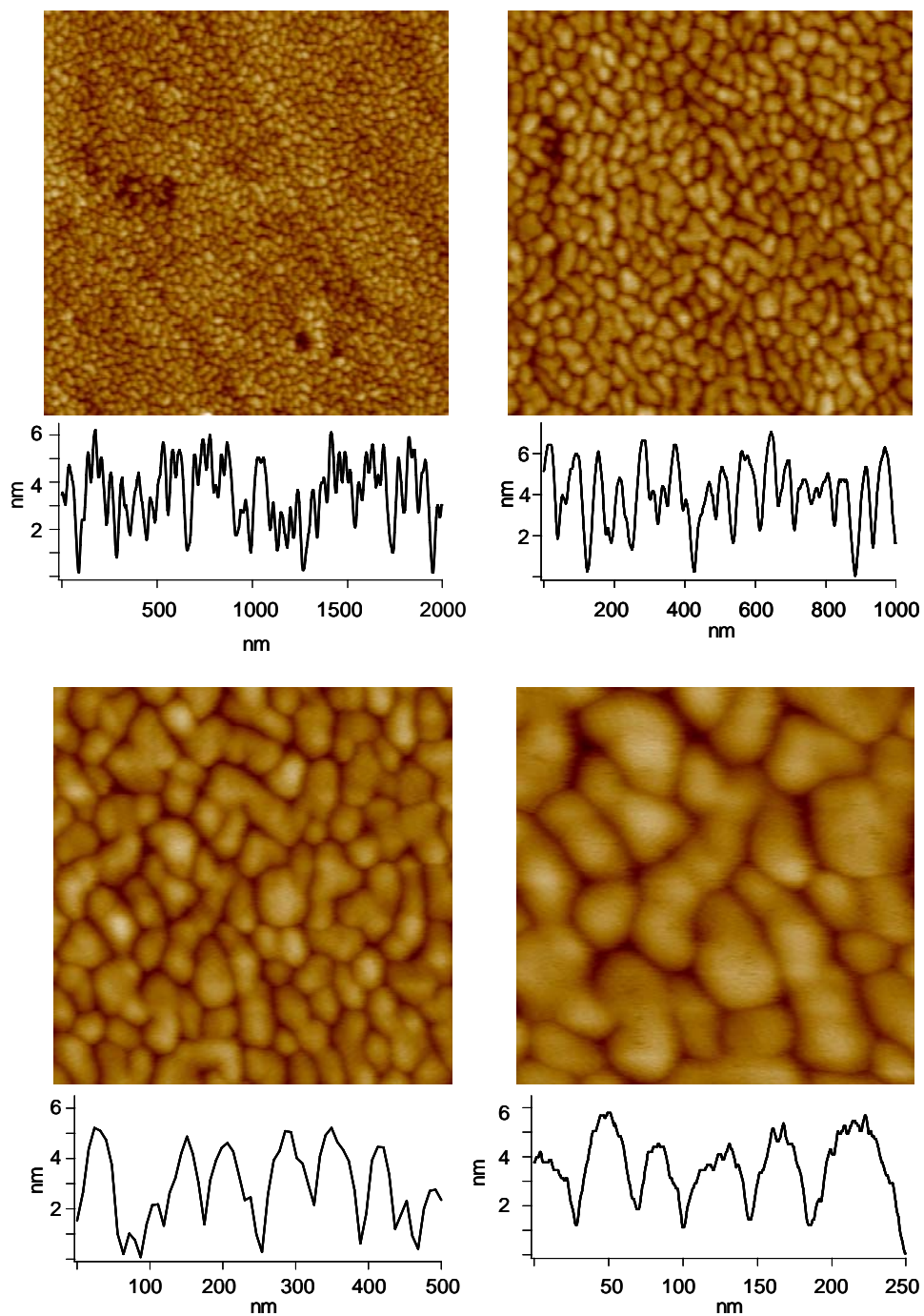
Gold colloids protected with motor **2** were prepared by using our previously reported procedure that produced motor-coated nanoparticles.⁴ The procedure is based on the method of Brust and Schiffrin.⁵ As with the preparation of the (2'*R*)-(M)-**2**-SAM, the dithioester **S2** was deprotected immediately before use. Treatment of (2'*R*)-(M)-**2** with tetraoctylammonium chloride and Au(III)chloride in a biphasic mixture of water and toluene with NaBH₄ generated gold colloids protected with the motor molecules. These were purified by precipitation from toluene/methanol mixtures. The ¹H NMR spectrum of the purified colloids showed only broad peaks, indicating that there was no appreciable free motor in solution.

Photochemical Experiments

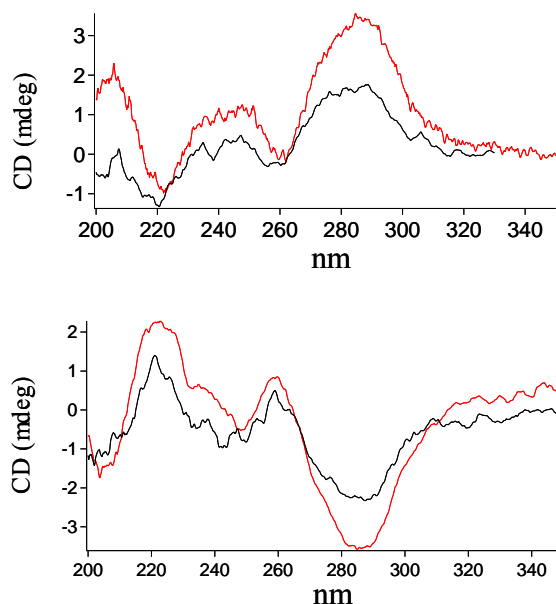
Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp at $\lambda_{\text{max}} = 365 (\pm 30)$ nm. Surfaces were first placed in a glass vial which was capped with a septum and then purged with argon for approximately 10 min. Samples were irradiated while in the argon-saturated glass vial at room temp. After irradiation samples were transferred to CD spectrometer in the dark.



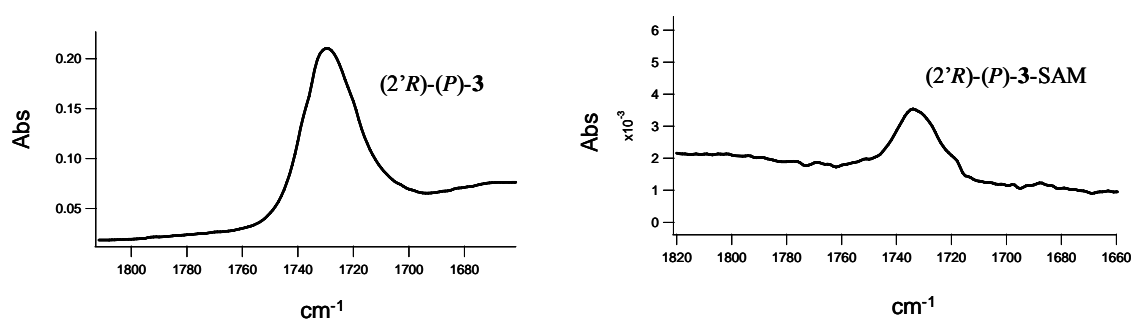
S1: UV-vis spectrum of semi-transparent gold film of approximately 5 nm on each side displays a plasmon band above 600 nm in accordance with a film of this thickness prepared on silanated quartz.⁶



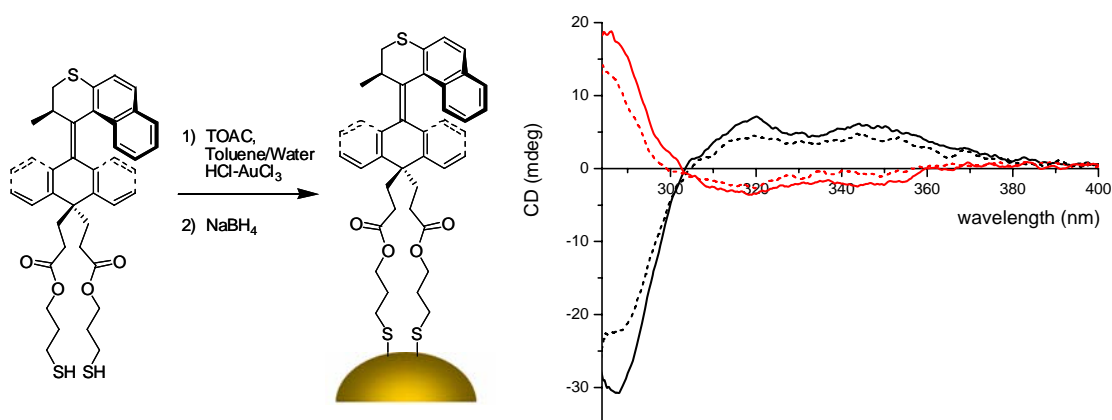
S2: Atomic force microscopy (AFM) topography images of semi-transparent gold film show islands of gold adhered to the quartz substrate in accordance with previously reported images.⁶



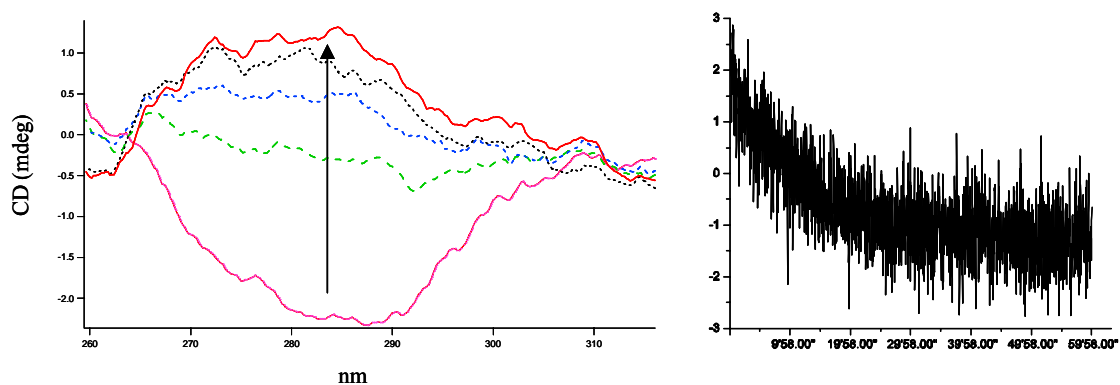
S3: Top: CD spectra of (2'*R*)-(P)-2-SAM (red) and (2'*R*)-(P)-2-mixed-dodecanethiol-SAM (black). Bottom: CD spectra of (2'*S*)-(M)-3-SAM (red) and (2'*S*)-(M)-3-mixed-dodecanethiol-SAM (black) (bottom).



S4: (A) ATR IR spectroscopy of free (2'*R*)-(P)-3 displaying the carbonyl at 1730 cm⁻¹. (B) Grazing angle IR spectra of the (2'*R*)-(P)-3-SAM on a semi-transparent Au film. The stretch at 1734 cm⁻¹ corresponds to the carbonyl in the “legs” of the motor.



S5: Gold colloids protected with motor (2'*R*)-(M)-**2** were prepared by the procedure of Brust and Schiffrin.⁵ CD spectroscopy shows that the motor can undergo rotary motion at the surface of the Au particles. Photochemical and thermal isomerization processes led to the expected change in the sign of the CD signals in comparison with the motor in solution.



S6: (a) Change in CD spectra of SAM on Au prepared from a solution of (2'*R*)-(M)-**3**:dodecanethiol 1:10 with irradiation time. Each spectrum taken after 15 min of irradiation. After 1 hour the photoisomerization was complete. (b) Time dependence of thermal decay of the signal at 285 nm at 80°C.

NMR Spectra

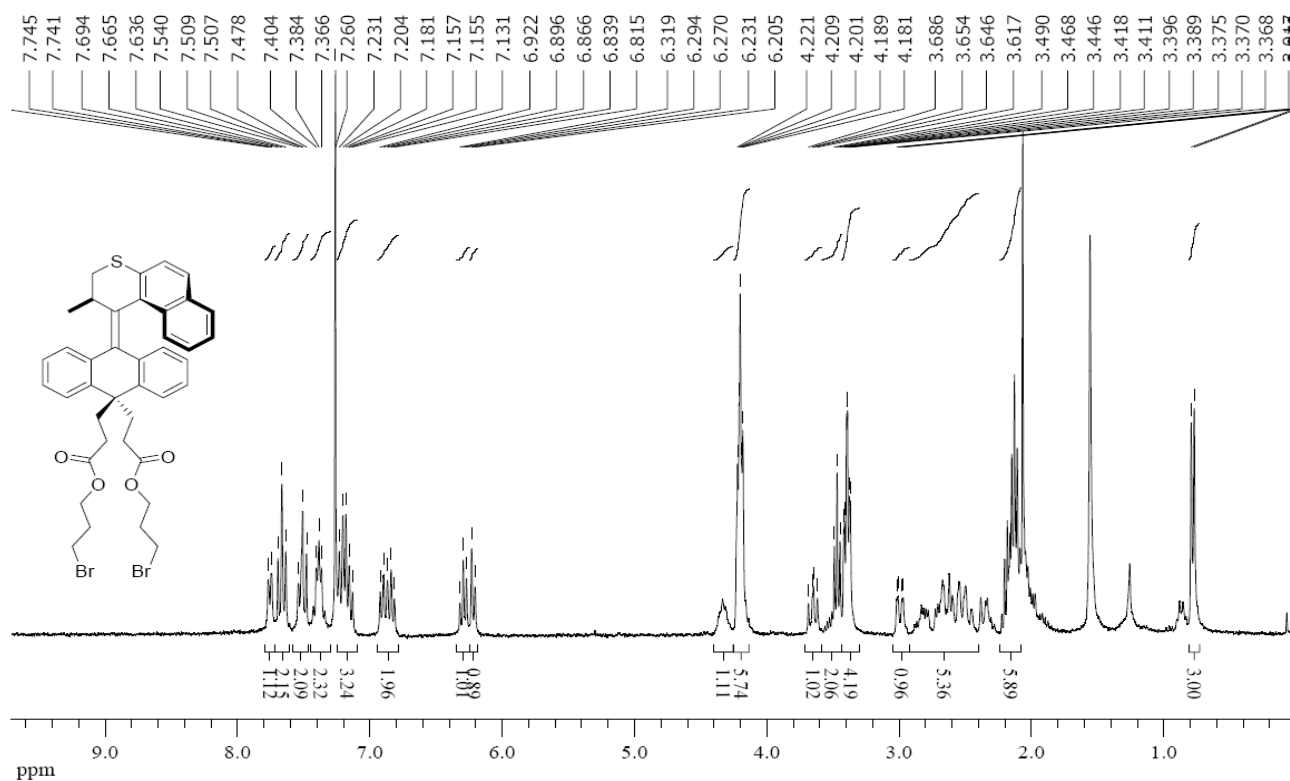


Figure 1. ^1H NMR spectrum of **S1** in CDCl_3 recorded at 300 MHz.

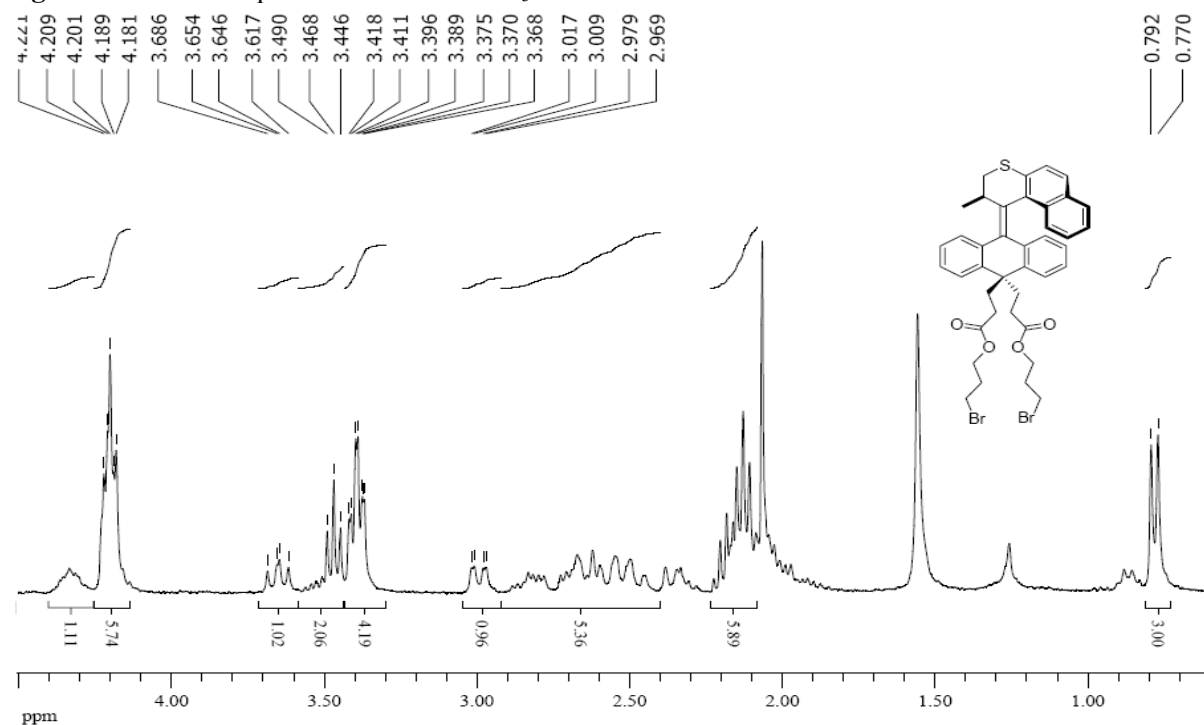


Figure 2. ^1H NMR spectrum of **S1** in CDCl_3 (expansion).

10

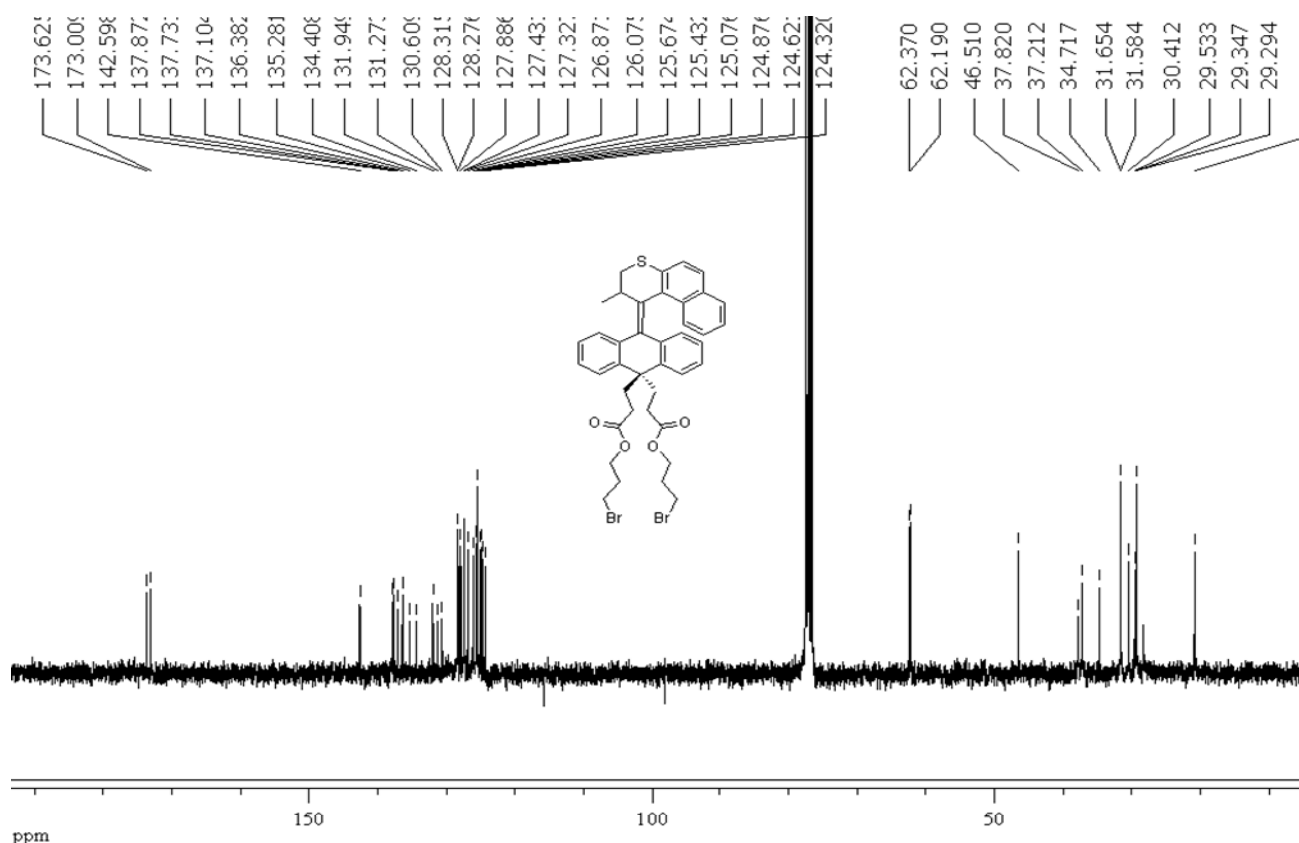


Figure 4. ¹³C NMR spectrum of **S1** in CDCl₃ taken at 75 MHz.

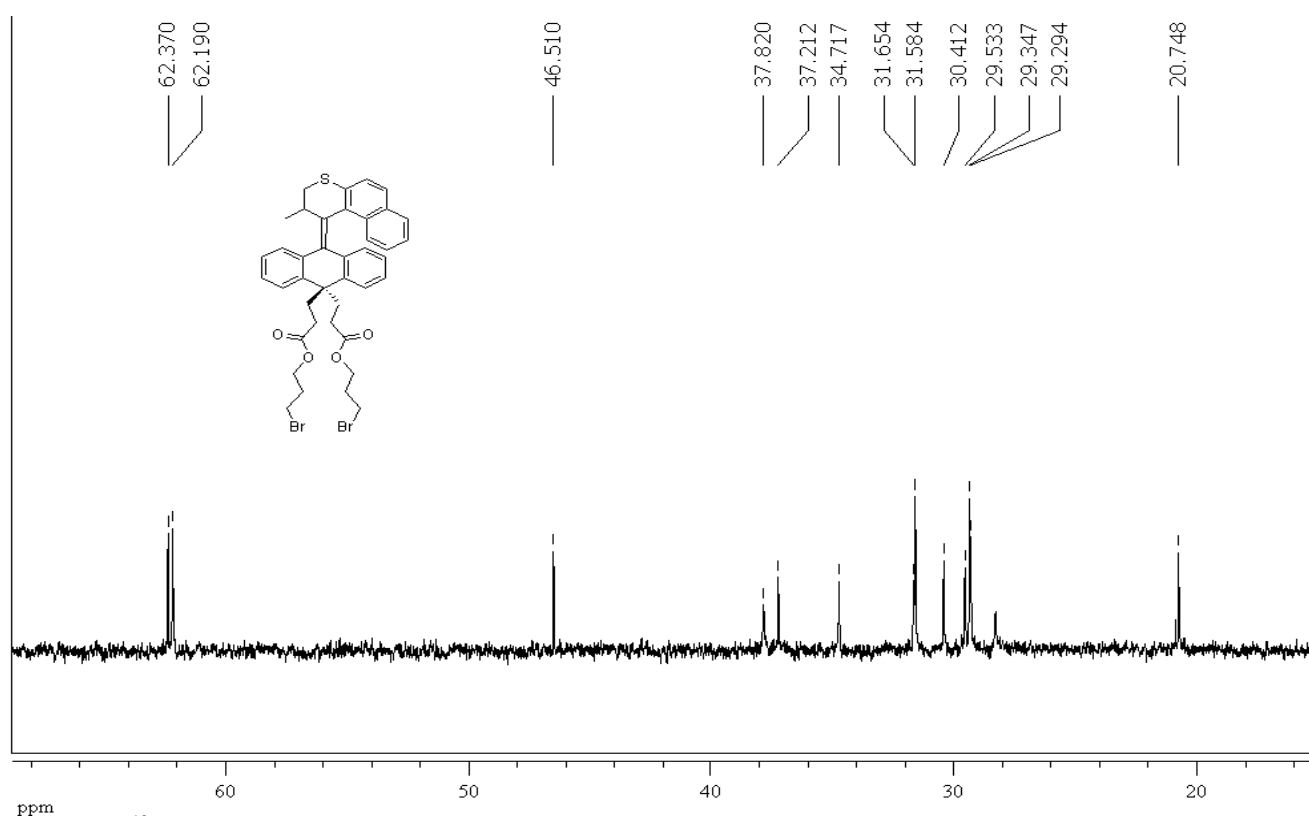


Figure 5. ¹³C NMR spectrum of **S1** in CDCl₃ taken at 75 MHz (expansion).

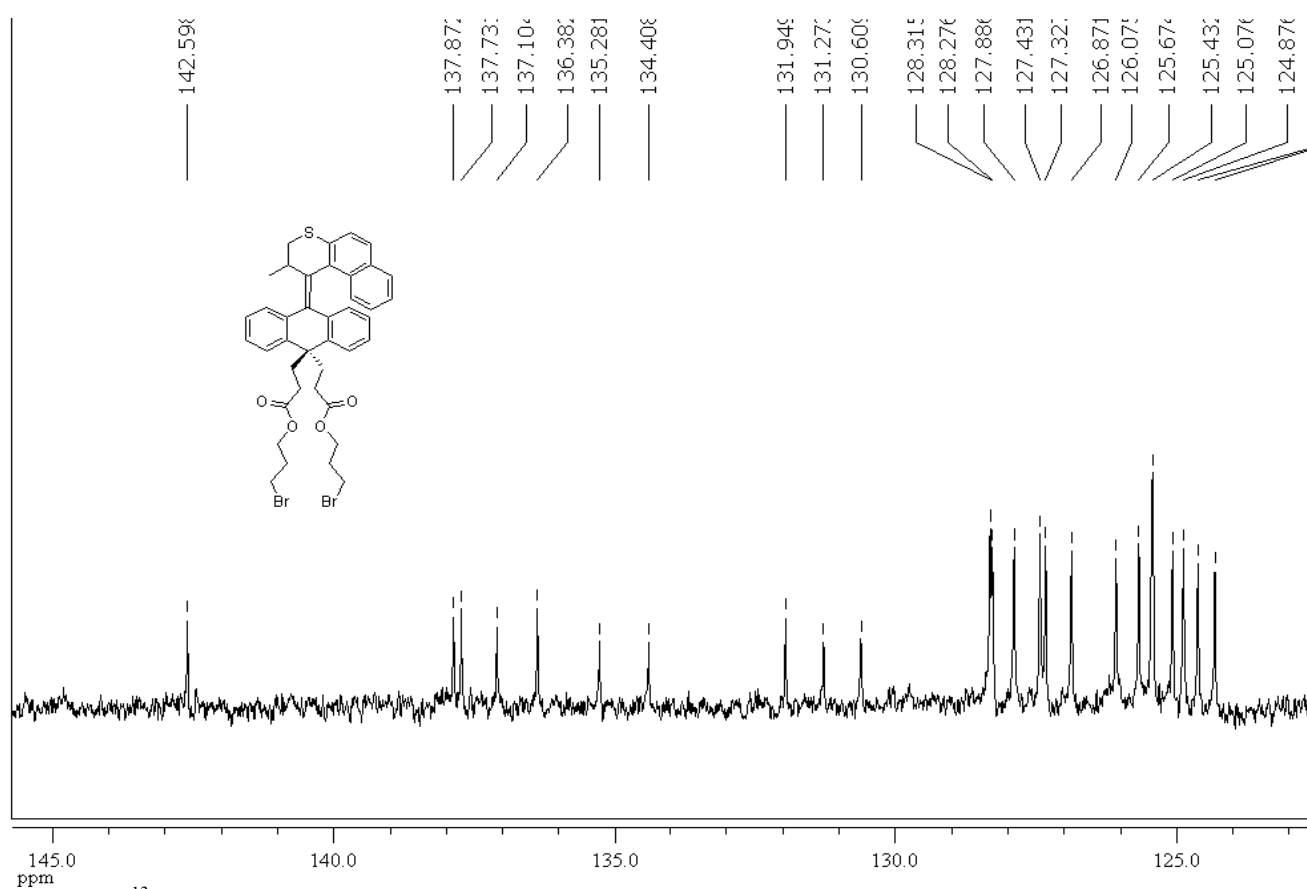


Figure 6. ¹³C NMR spectrum of S1 in CDCl₃ taken at 75 MHz (expansion).

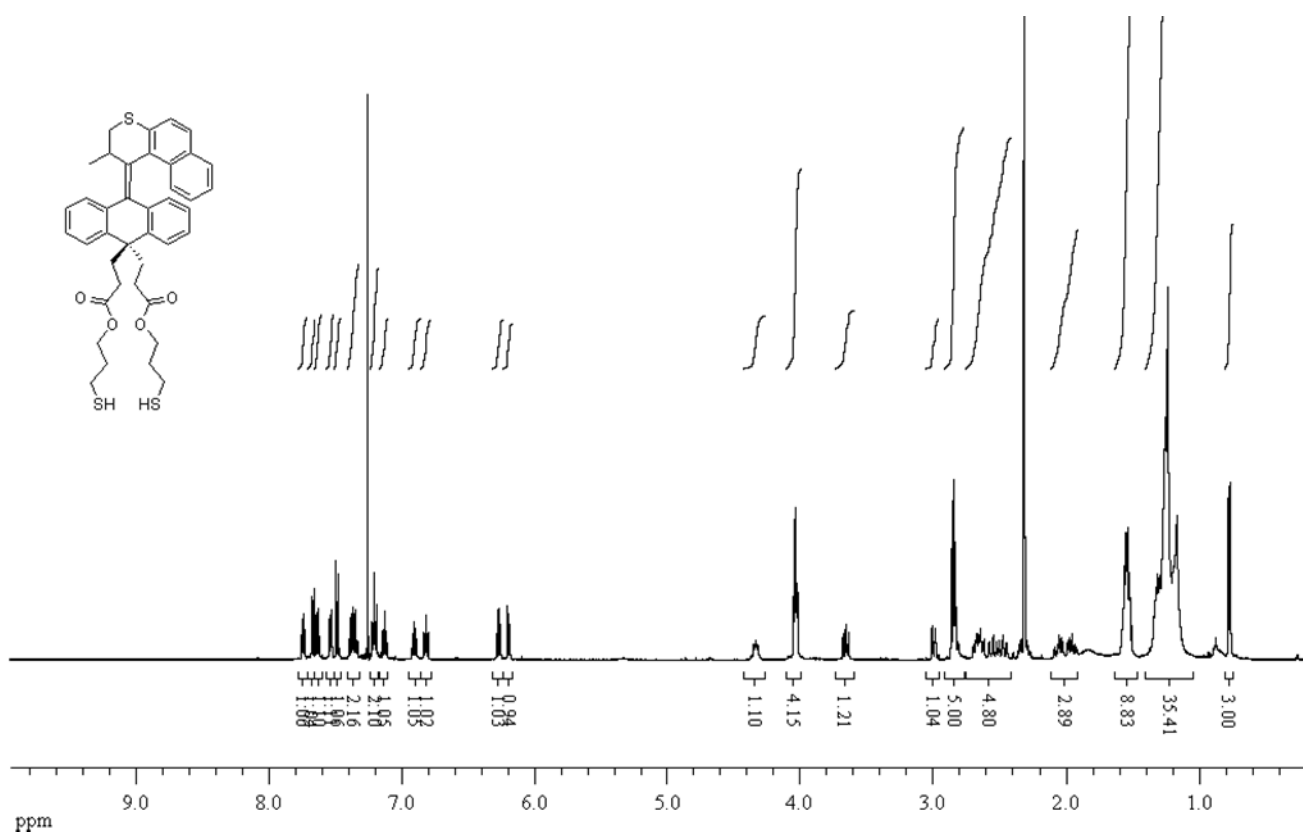


Figure 7. ^1H NMR spectrum of deprotected **S2** in CDCl_3 (expansion).

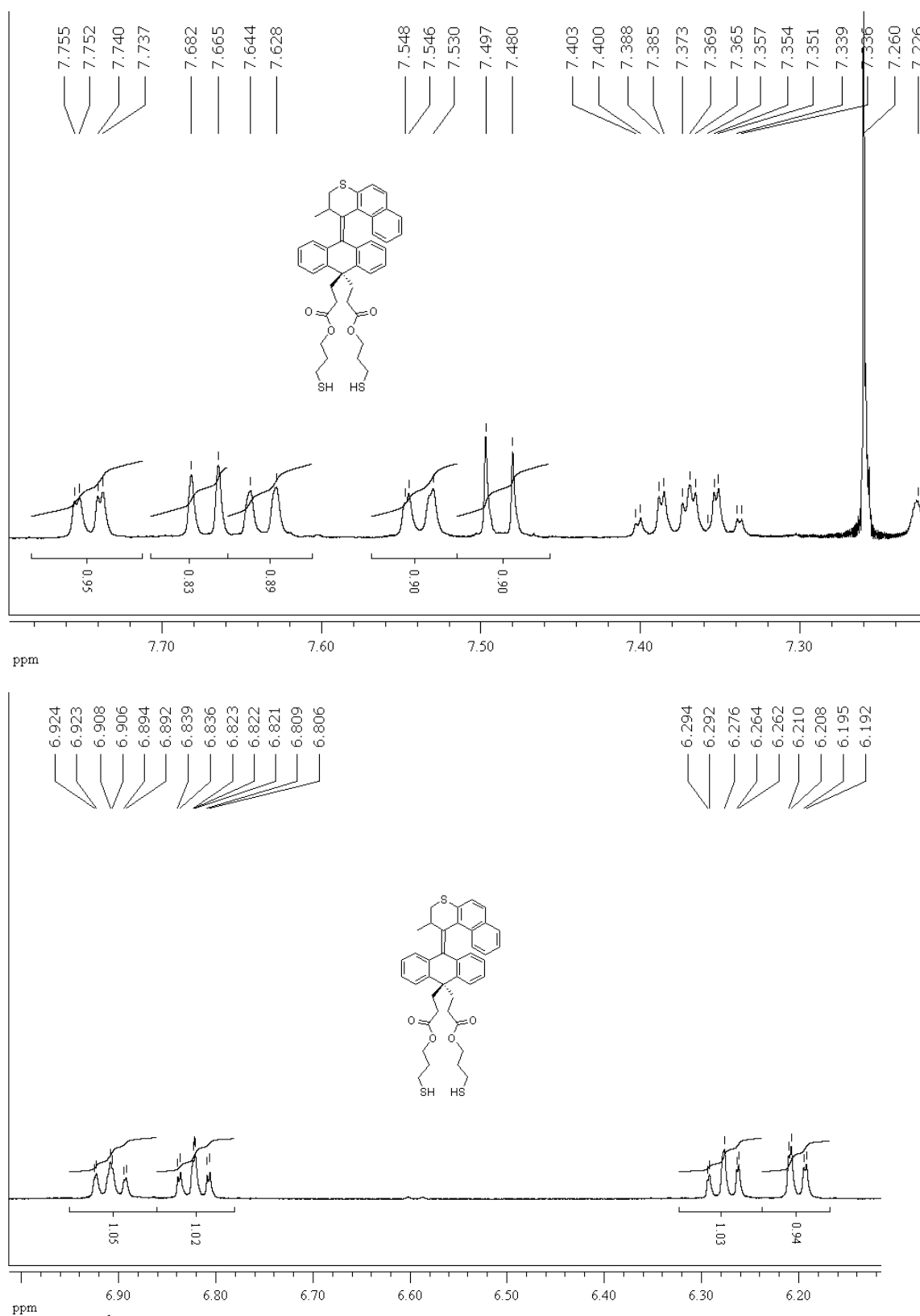


Figure 8. ^1H NMR spectrum of deprotected **S2** in CDCl_3 (expansion).

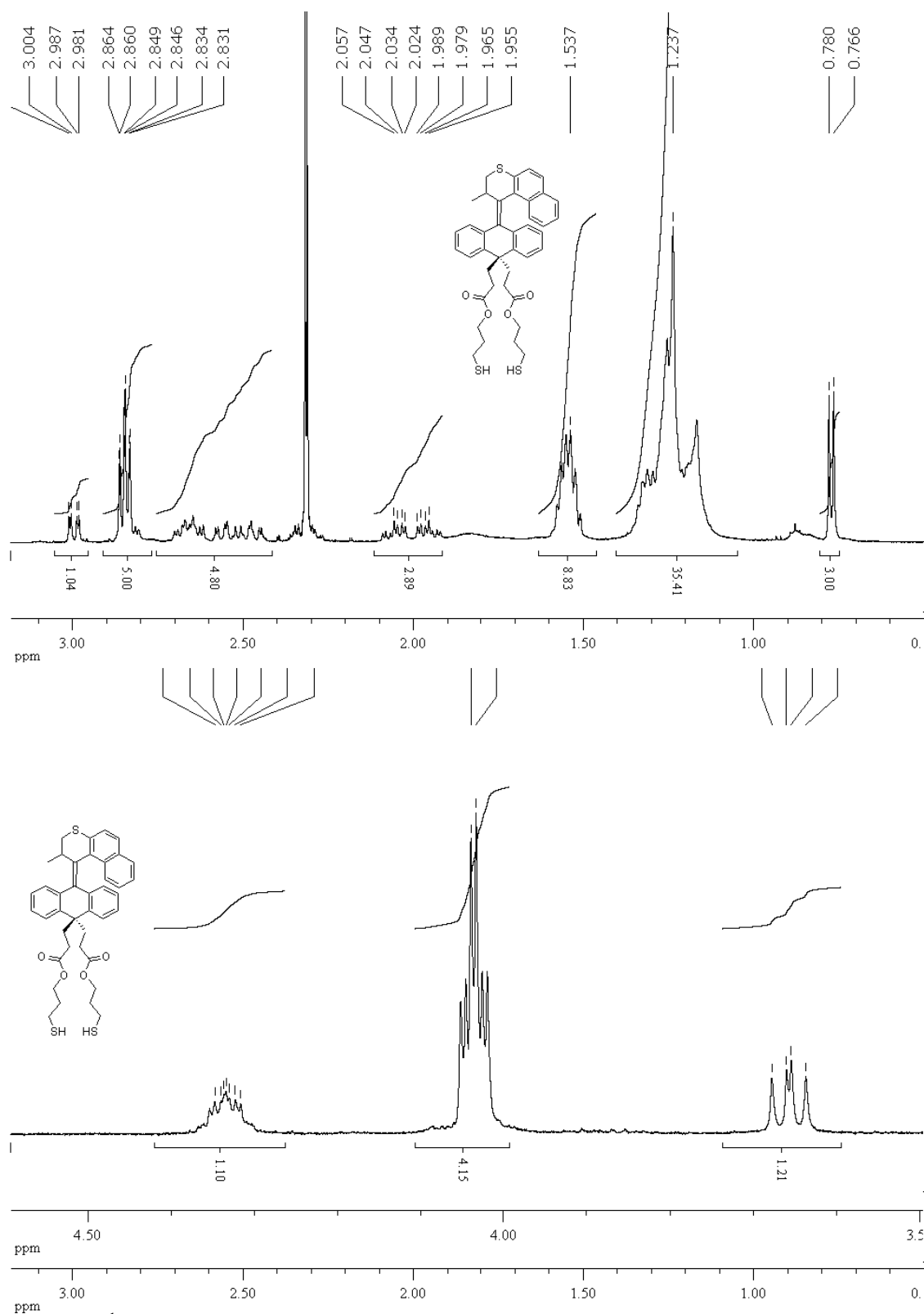


Figure 9. ^1H NMR spectrum of deprotected S2 in CDCl_3 (expansion).

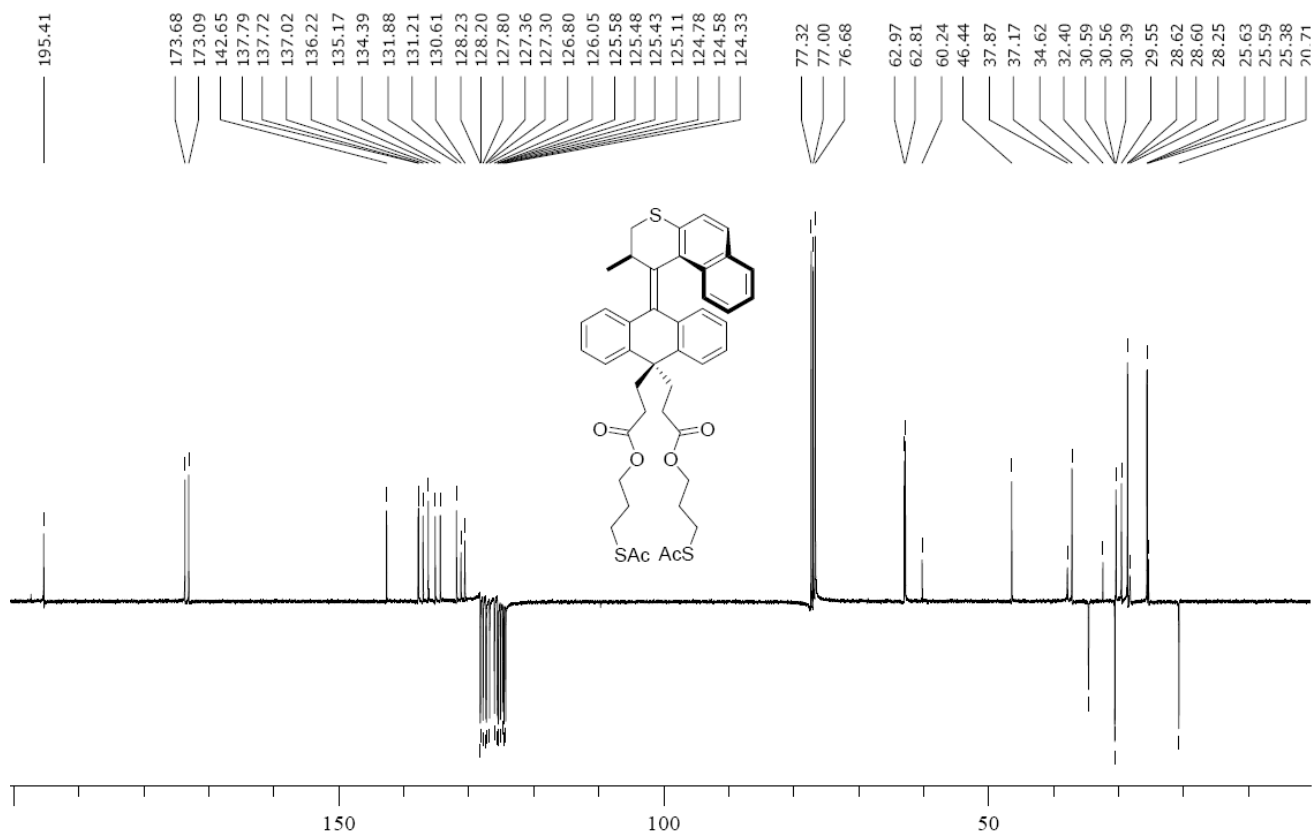


Figure 10. ^{13}C NMR spectrum of **S2** in CDCl_3 taken at 100 MHz.

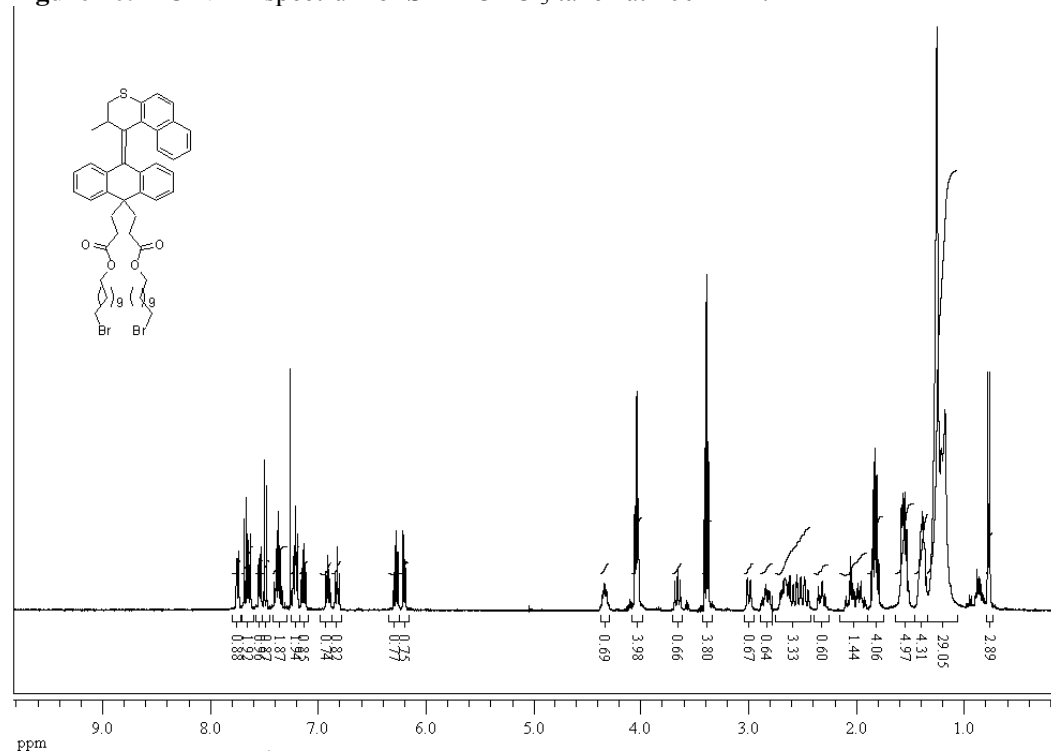


Figure 11. 400 MHz ^1H NMR spectrum of **S3** in CDCl_3 (expansion).

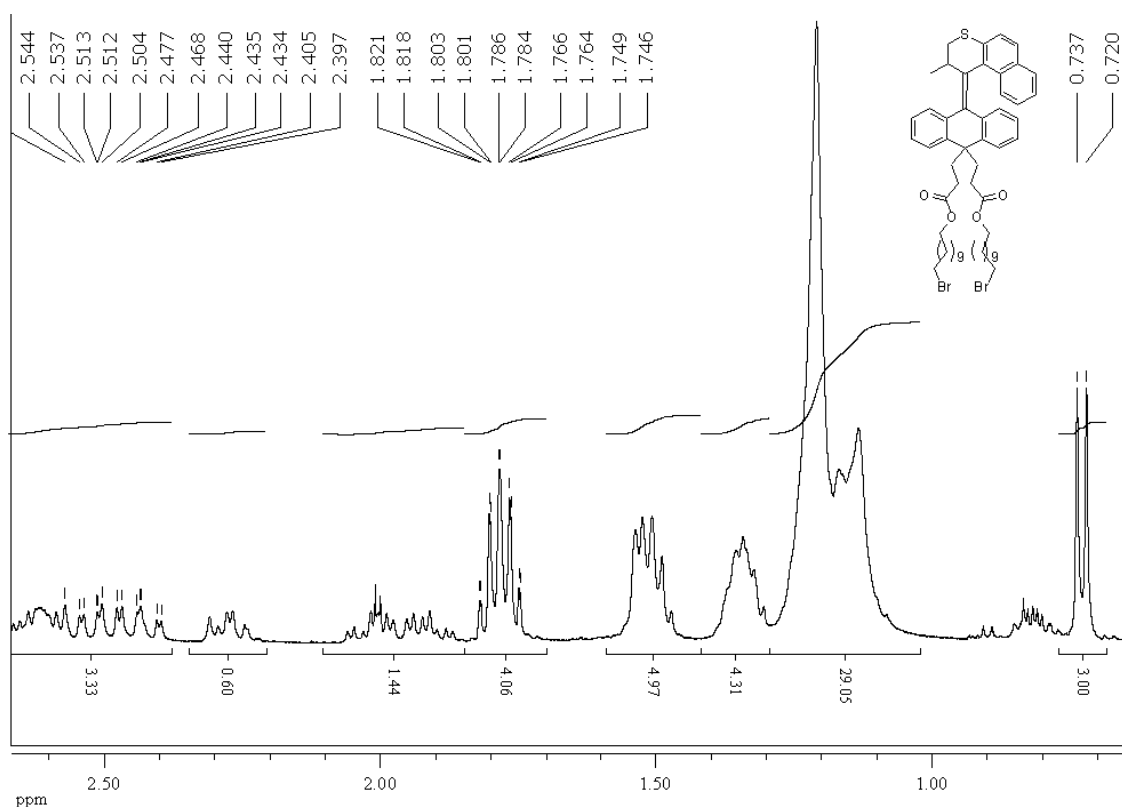


Figure 12. 400 MHz ^{13}C NMR spectrum of **S3** in CDCl_3 (expansion).

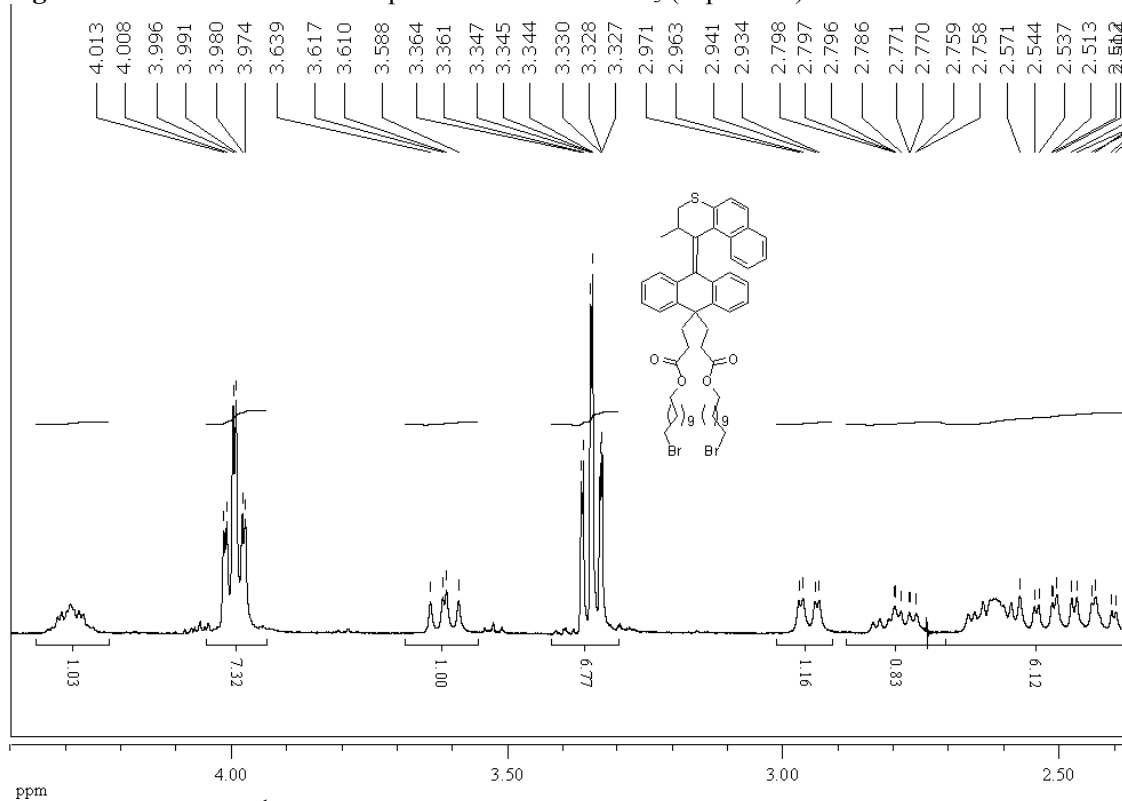


Figure 13. 400 MHz ^1H NMR spectrum of **S3** in CDCl_3 (expansion).

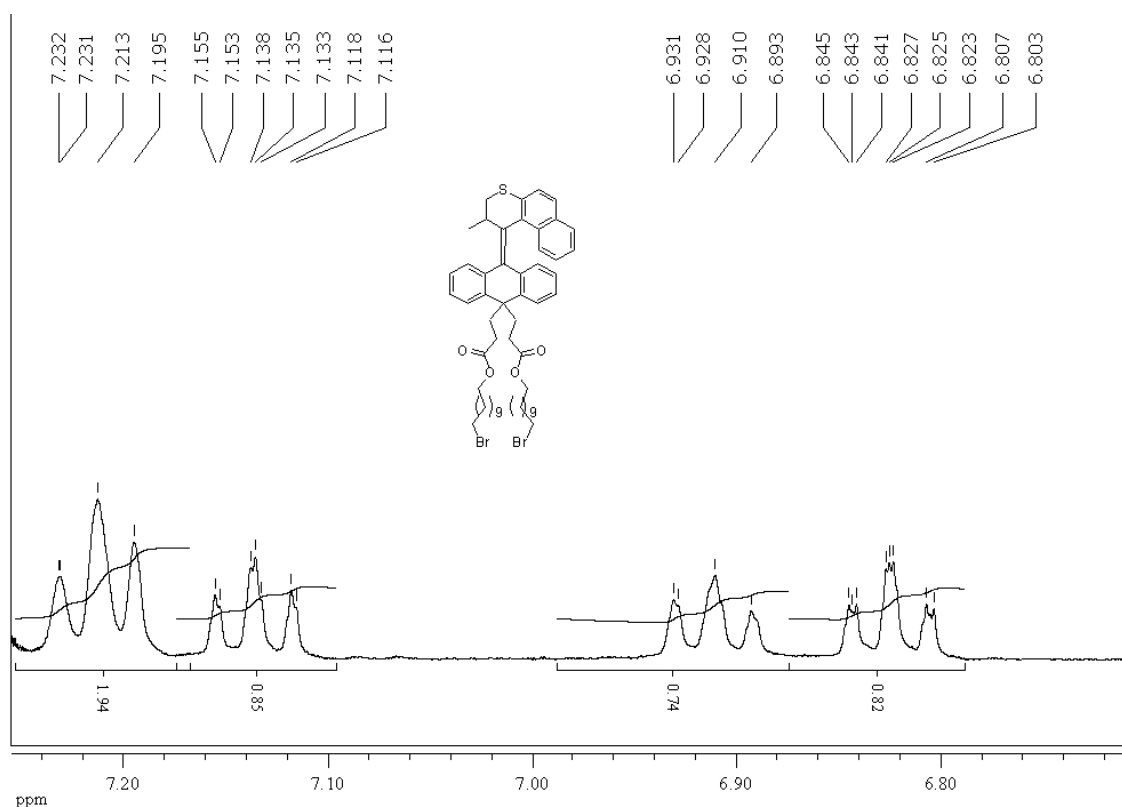


Figure 14. 400 MHz ^1H NMR spectrum of **S3** in CDCl_3 (expansion).

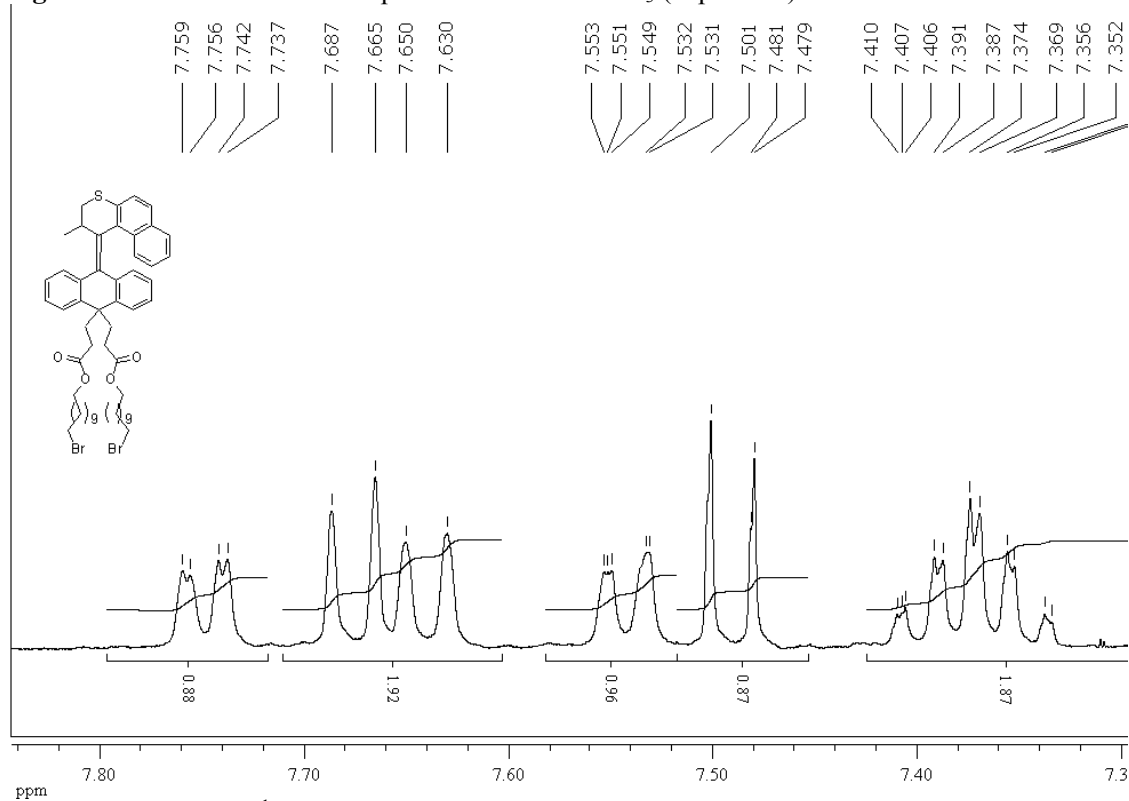


Figure 15. 400 MHz ^1H NMR spectrum of **S3** in CDCl_3 (expansion).

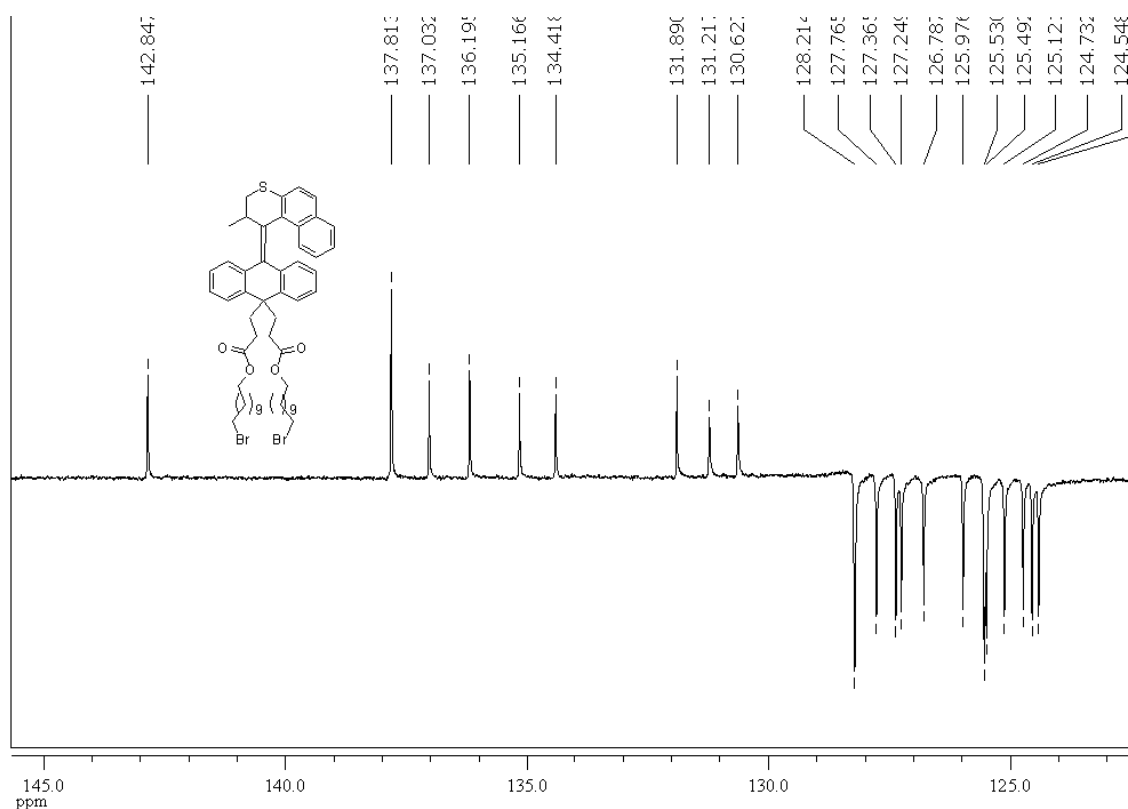


Figure 18. 400 MHz ^{13}C NMR spectrum of **S3** in CDCl_3 (expansion).

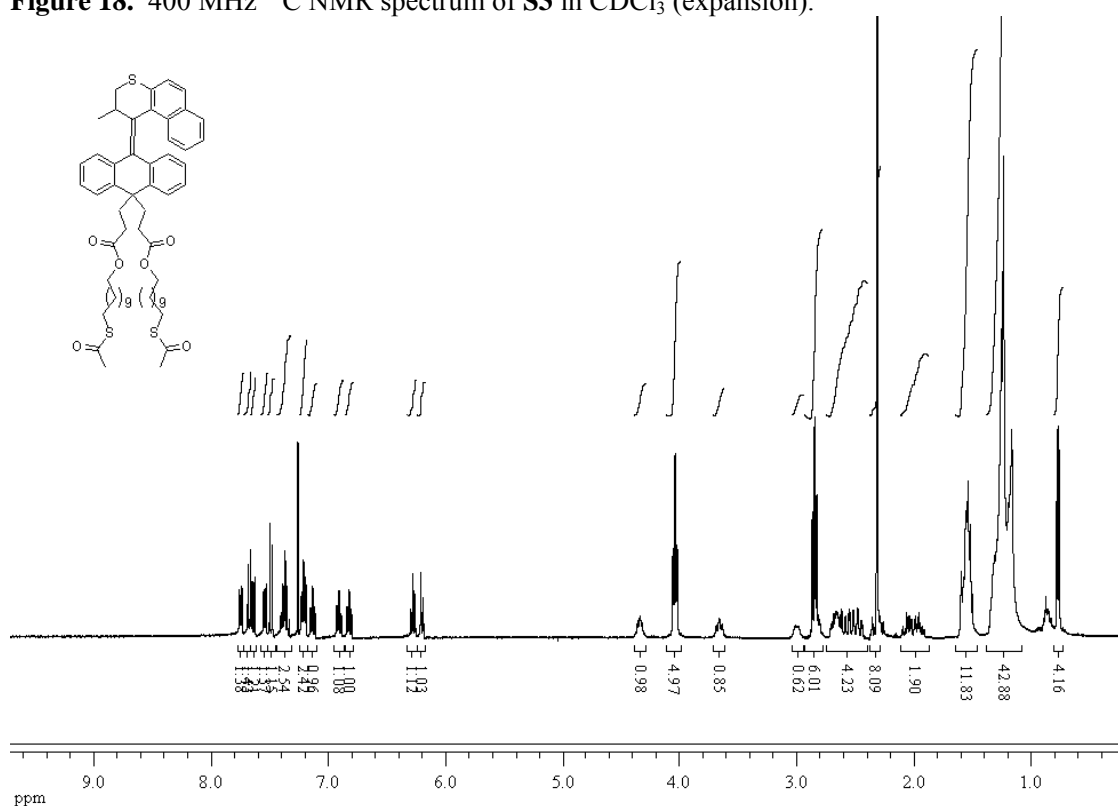


Figure 19. ^1H NMR spectrum of **S4** in CDCl_3 taken at 400 MHz.

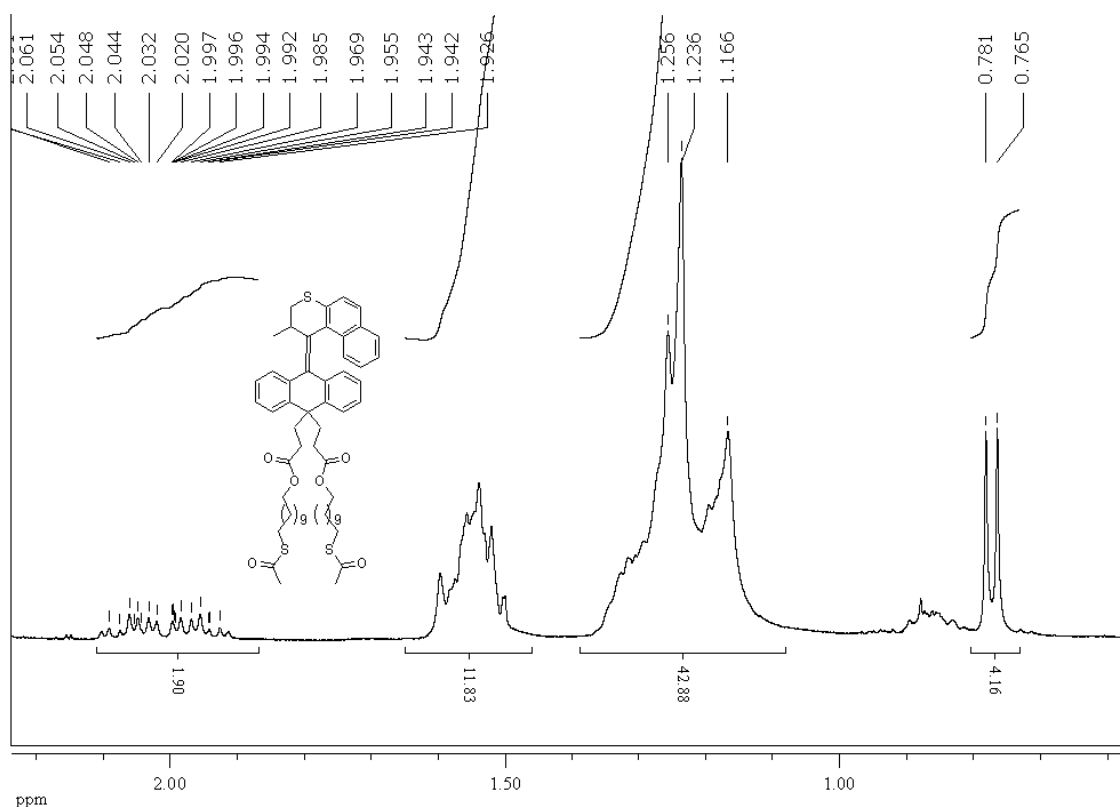


Figure 20. ^1H NMR spectrum of **S4** in CDCl_3 taken at 400 MHz (expansion).

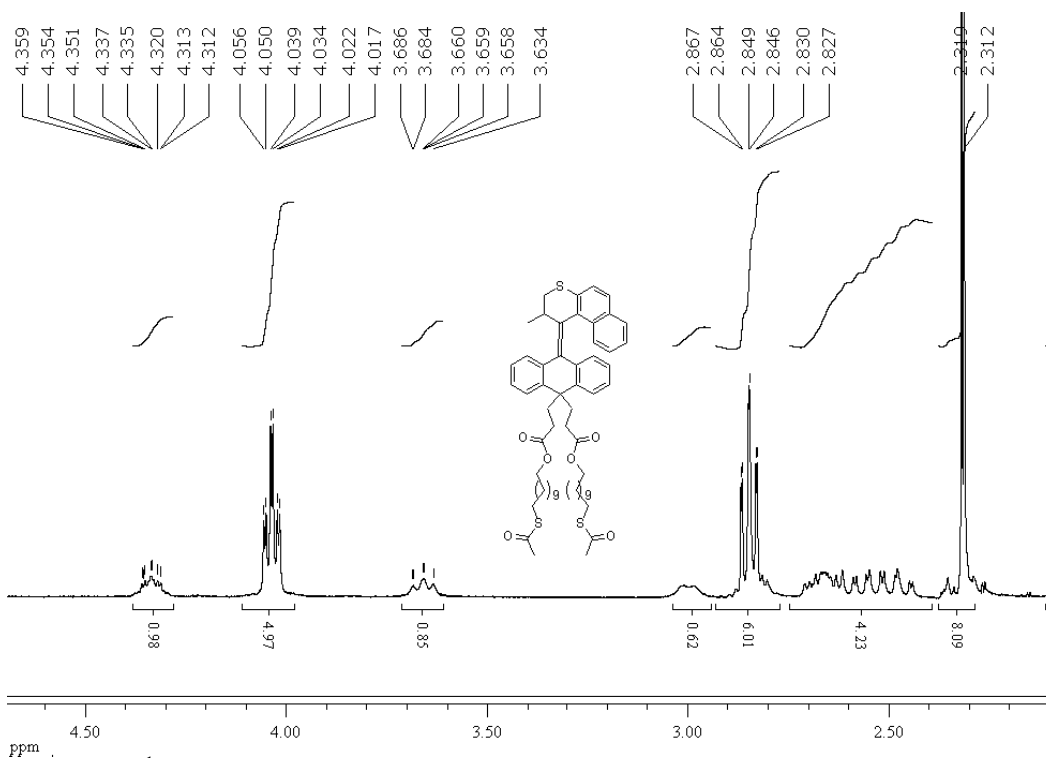


Figure 21. ^1H NMR spectrum of **S4** in CDCl_3 taken at 400 MHz (expansion).

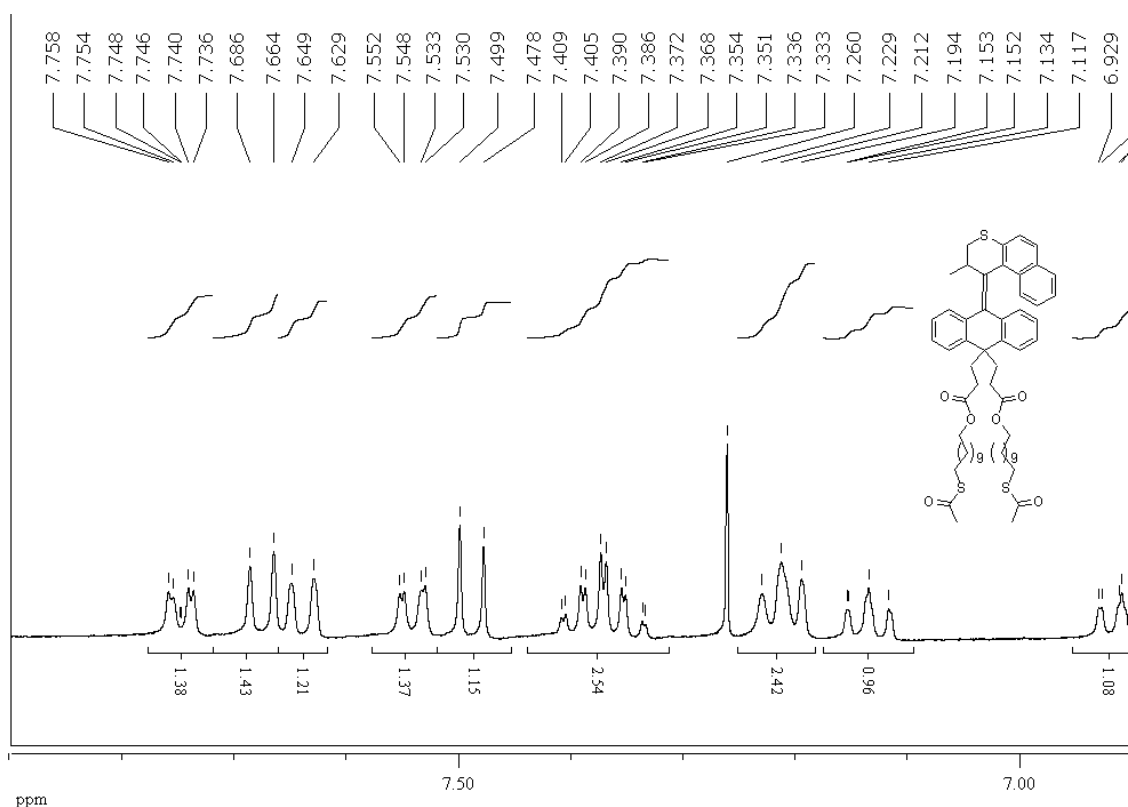


Figure 22. ¹H NMR spectrum of **S4** in CDCl₃ taken at 400 MHz (expansion).

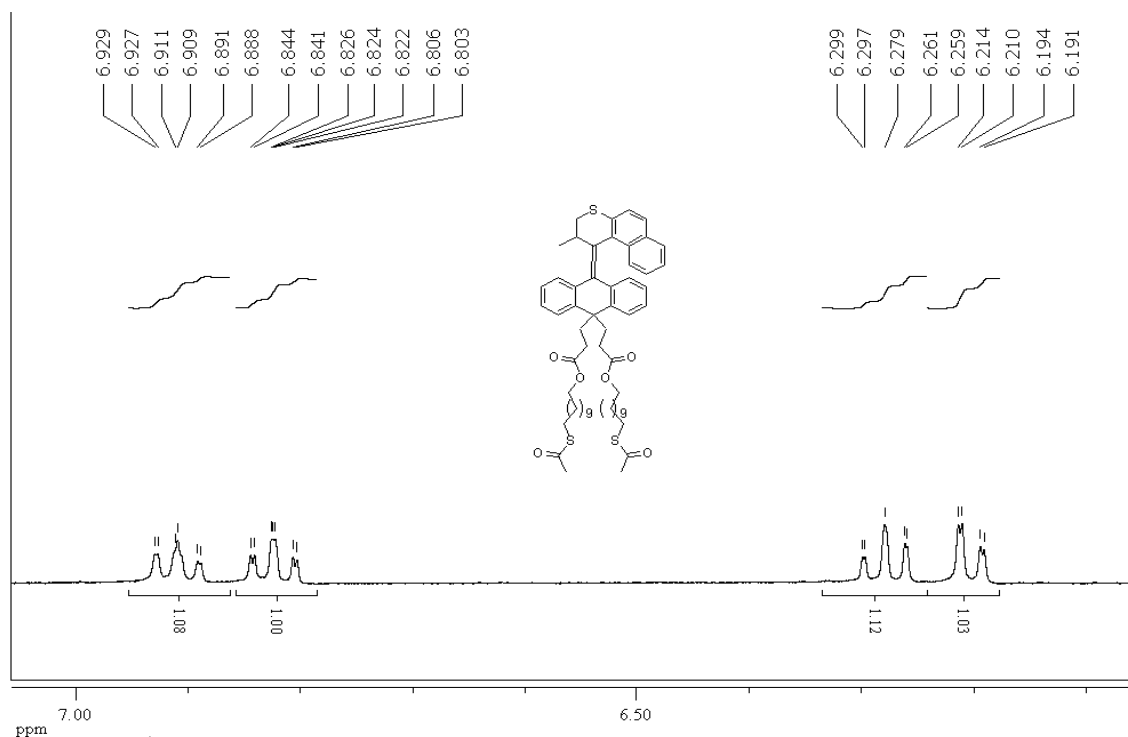


Figure 23. ¹H NMR spectrum of **S4** in CDCl₃ taken at 400 MHz (expansion).

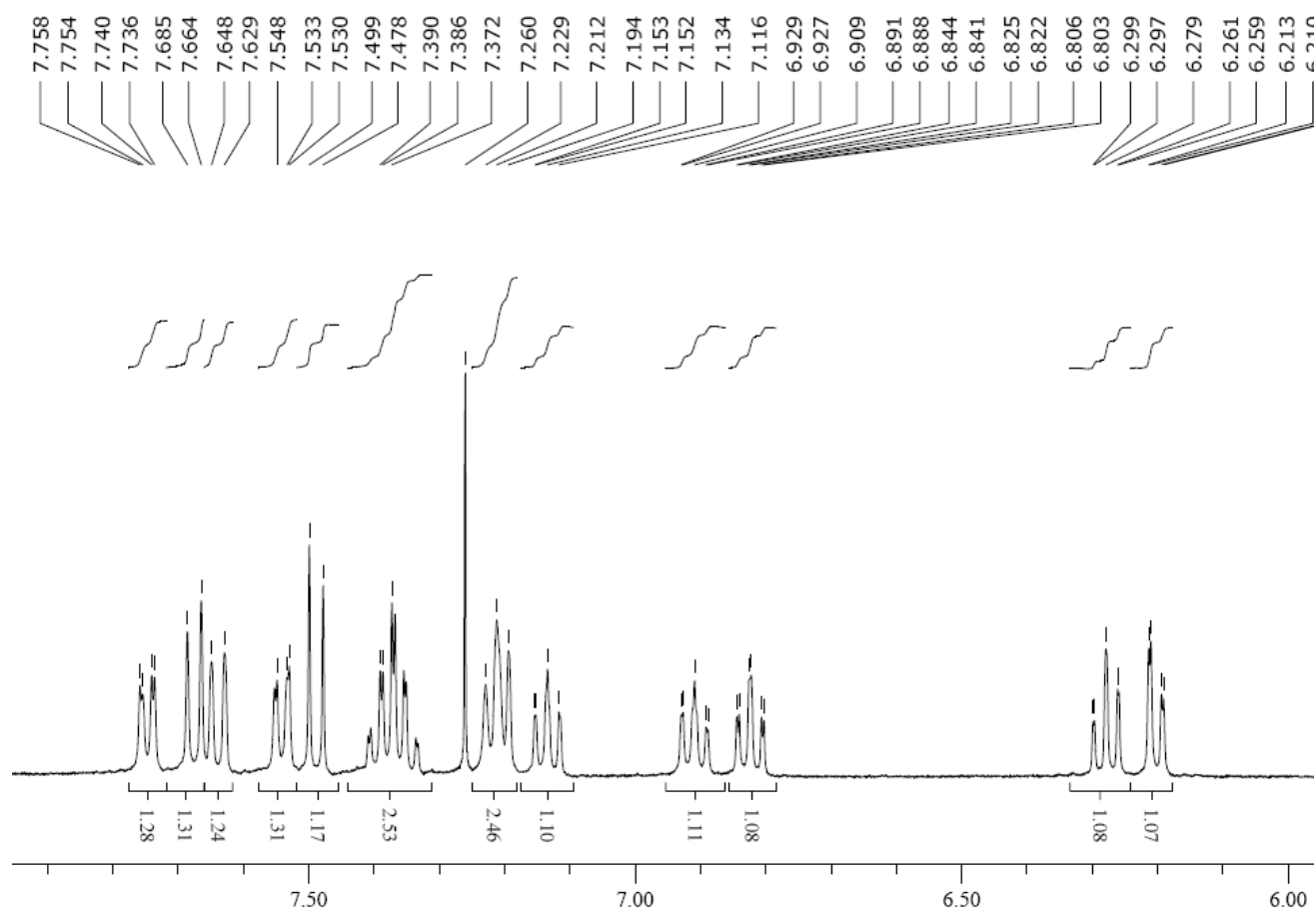


Figure 24. ^1H NMR spectrum of **S4** in CDCl_3 taken at 400 MHz (expansion).

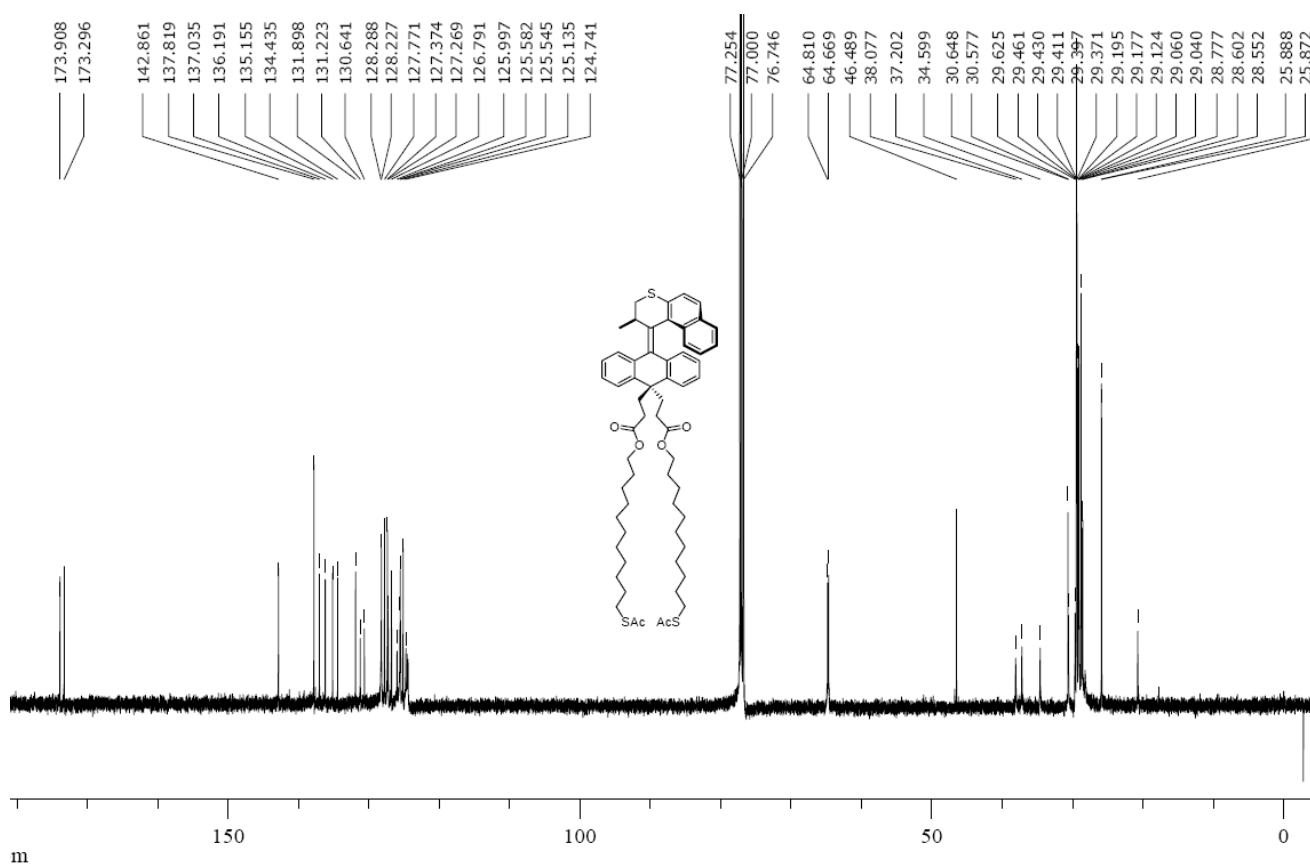


Figure 25. ¹³C NMR spectrum of **S4** in CDCl₃ taken at 125 MHz.

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